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(54) Procedure for the Combinatorial Production and Testing of Heterogeneous Catalysts

(57) The array of heterogeneous catalysts and/or their precursors comprising a body having preferably parallel, continuous channels and in which at least n channels contain n different heterogeneous catalysts and/or their precursors, wherein n is at least 2, preferably 10, and particularly preferably 1000, especially 10000.

A process for the production of the array comprising the following steps:

a1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursor and possibly of dispersions of inorganic carrier materials,
a2) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the solutions, emulsions and/or dispersions,
a3) simultaneous or successive coating of the channels of the body with the solutions, emulsions and/or dispersions, where into each channel, a predefined quantity of the solutions, emulsions and/or dispersions is added to obtain a predefined composition, and
a4) possibly the heating of the coated body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

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Description

The invention concerns a procedure for the combinatorial production and testing of heterogeneous catalysts and catalysts obtain by using this procedure.

For the production and testing of new chemical compounds, in addition to classical chemistry, which is aimed at the synthesis and testing individual of substances, the so-called combinatorial chemistry has developed. In this case, a large number of reagents are initially converted during a one-pot synthesis and tested whether the resulting reaction mixture displayed the desired properties, e.g. a pharmacological effect. In case such a reaction mixture was found to be effective, it was necessary to determine, during a subsequent step, which special substance in the reaction mixture was responsible for such effect. In addition to the complicated process of determining the actual active compound, it was also difficult to exclude undesired side reactions in the presence of a large number of reagents.

In another approach of combinatorial synthesis, a large number of compounds was synthesized through targeted dosing and conversion of a number of reagents in a large number of different reaction vessels. In this procedure, each reaction vessel preferably contains a conversion product so that, e.g. in case a mixture is found to have a pharmacological effect, the base substances used in its production are immediately identified.

In addition to the initial applications of such more specific combinatorial synthesis in the search for new pharmacologically active substances, such synthesis procedure was recently also extended to low-molecular organic compounds as well as organic and inorganic catalysts.

In "Phosphatase Catalysis Developed via Combinatorial Organic Chemistry", J. Org. Chem. 1995, 60, pages 6666 through 6667, F. M. Menger et al. describe the production of organic catalysts by using combinatorial procedures. Eight different functionalized carboxylic acids were attached to a polyallyl amine via amide bonds. In addition, different metal ions were attached to the polymers through complex formation. The resulting polymers were then tested for their phosphatase activity. The description does not specify whether the catalysts were produced in an automated production process; only the production of individual catalysts is described.

C. L. Hill, R. D. Gall, "The first combinatorially prepared and evaluated inorganic catalysts. Polyoxometalates for the aerobic oxidation of the mustard analog tetrahydrothiophene (THT)", J. Mol. Catalysis A: Chemical 114 (1996), pages 103 through 111, describe the combinatorial production and testing of polyoxometalates for the aerobic oxidation of tetrahydrothiophene. The polyoxometalates were produced by mixing different percentages of metal salt solutions of the desired metals. For that purpose, wolframate, molybdate and vanadate solutions as well as a sodium hydrogen phosphate solution were prepared. After dosing the corresponding solutions, the pH value was set to a predefined value, and a conversion was triggered. The catalysts obtained were used in the conversion in dissolved form. The description does not

specify whether the catalysts were produced in automated form.

Procedures for the targeted dosing of different quantities of different liquid reagents in an array of reaction vessels, which may e.g. resemble a spotting plate, are described in US 5,449,754. The ink head of an ink jet printer connected with supply solutions of the reagents is moved by means of an XY positioner over the array, and the discharge of the liquids is controlled by means of a computer.

F. C. Moathes et al, "Infrared Thermographic Screening of Combinatorial Libraries of Heterogeneous Catalysts", Ind. Eng. Chem. Res. 1996, 35, pages 4801 through 4803, describe the testing of combinatorially produced libraries of heterogeneous catalysts through IR testing. The catalysts consisted of different elemental metals applied to aluminum oxide which were tested in terms of the catalytic activity of hydrogen oxidation. The individual catalysts were prepared by submerging aluminum oxide pellets in corresponding metal salt solutions, followed by drying and calcination. The description did not specify whether the catalysts were produced in an automated manner or not.

The different pellets were placed in predefined positions on a carrier and contacted with hydrogen under reaction conditions. In the event of catalytic activity, the catalyst heats up, and the increase in temperature was measured by means of an IR camera, which made it possible to determine the active catalysts.

In B. E. Baker et al, "Solution-Based Assembly of Metal Surfaces by Combinatorial Methods", J. Am. Chem.-Soc. 1996, 118, pages 8721 through 8722, the production of metal surfaces with different compositions by using combinatorial procedures is described. A silane-coated glass plate is dipped into a colloidal gold solution at a predetermined speed to produce a gradient of gold distribution on the substrate. After removing and drying the plate, it is rotated by 90° and dipped into a silver ion solution to produce another concentration gradient on the plate. This results in a continuous change in the composition on the surface.

X.-D. Xiang et al., "A Combinatorial Approach for Materials Discovery", Science 268 (1995), pages 1738 through 1740, describe the production of BiSrCaCuO and YBaCuO-supraconductor films on substrates wherein, through physical masking procedures and vapor deposition techniques, during separation of the corresponding metals, a combinatorial array of different metal compositions is obtained. After calcination, in different positions of the array, there are different compositions, which can be tested with microprobes, for example in terms of conductivity.

WO 96/11878 also describes, in addition to the production of such supraconductor arrays, the production of zeolithes, wherein an ink jet is used to dose the required quantities of several metal salt solutions without mixing to a kind of spotting plat- and the addition of the last solution causes a precipitation. BSCCO supraconductors can also be produced by separately dosing the individual nitrate solutions of the required metals by spraying them onto a type of spotting plate and heating them afterwards.

The prior art procedures can be used to produce different heterogeneous catalysts. Testing the catalysts, however, is often complicated and can not be performed under real-life conditions, e.g. with the required residence times of the reagents on the catalyst, since the catalysts are present, for example, on a larger, generally flat carrier to which, for a example, a gas mixture to be converted needs to be applied.

The object of this present invention is to provide a procedure for the production of arrays of inorganic heterogeneous catalysts or their precursors, wherein the resulting catalysts can be tested with less effort and under conditions that are similar to large-scale technical procedures. In addition, the disadvantages of existing systems are to be avoided. The corresponding arrays are also to be provided.

According to this present invention, this is achieved by providing an array of heterogeneous catalysts and/or their precursors, preferably inorganic heterogeneous catalysts and/or their precursors, consisting of a body with continuous channels, preferably parallel continuous channels, with at least n channels containing n different, preferably inorganic, heterogeneous catalysts and/or their precursors, wherein n is at least 2, preferably 10, and particularly preferably 1000, and especially 10000.

In one embodiment of this present invention, the body is a tube bundle reactor or heat exchanger, and the channels are tubes.

In another embodiment of this present invention, the body is a block made from solid material in which the channels are located, for example in the form of boreholes.

The heterogeneous catalysts and/or their precursors are preferably full contacts or carrier catalysts and/or their precursors and are present in bulk form, as a tube wall coating or auxiliary carrier coat.

The term "array of inorganic heterogeneous catalysts or their precursors" refers to an arrangement of different inorganic heterogeneous catalysts or their precursors on predetermined, spatially separate areas of a body, preferably of a body with parallel continuous channels, preferably of a tube bundle reactor or heat exchanger. The geometrical arrangement of the individual areas to each other can be freely chosen. For example, the areas can be arranged in a row (quasi one-dimensional) or in the form of a chessboard pattern (quasi two-dimensional). In the case of a body with parallel continuous channels, preferably a tube bundle reactor or a heat exchanger with a large number of tubes running parallel to each other, the arrangement becomes clear upon viewing a cross-sectional surface perpendicular to the longitudinal axis of the tubes: the result is a surface where the individual tube cross sections reflect the different areas arranged at a spatial distance from each other. The areas or tubes can - for example in the case of tubes with a circular cross section – also be arranged tightly bundled, so that different rows of areas are provided in a staggered arrangement.

The term "body" refers to a three-dimensional object having a multitude of (at least n) continuous channels. The channels therefore connect two surface areas of the body and run through the body. Preferably, the channels run largely, preferably completely, parallel to each other. The body can consist of one or several materials and be solid or hollow. The body can have any suitable geometrical shape. Preferably, the body has two surfaces running parallel to each other, each having one opening of the channels. The channels run preferably perpendicular to such surfaces. One example for such a body is a cuboid or cylinder in which the channels run between two parallel surfaces; however, a multitude of similar geometries is also conceivable.

The term "channel" refers to the connection between two openings on the body surface running through the body which permits, for example, a fluid to pass through the body. The channel can have any geometry. The channel may have a profile which varies over the length of the channel or preferably a constant channel profile. The channel profile may, for example, have an oval, round or polygonal circumference with straight or curved connections between the corner points of the polygon. A round or equilateral polygonal cross section is preferred. Preferably, all channels in the body have the same geometry (in terms of cross section and length) and run parallel to each other.

The terms "tube bundle reactor" and "heat exchanger" refer to bundled parallel arrangements of a large number of channels in the form of tubes, wherein the tubes may have any cross section. The tubes are arranged in a permanent spatial relationship with each other, are preferably provided at a spatial distance from each other, and are preferably covered by a jacket which encloses all tubes. This makes it possible to conduct e.g. a heating or cooling medium through the jacket to ensure that the temperature of all tubes is uniformly controlled.

The term "block consisting of a solid material" refers to a body made from a solid material (which, in turn, may consist of one or several base materials), in which the channels are provided, for example in the form of boreholes. The geometry of the channels (boreholes) can be freely chosen, as described above for the channels in general. The channels (boreholes) need not be created through drilling, but may also be recessed, e.g. during molding of the solid body/block, for example through extrusion of an organic and/or inorganic molding material (for example through a suitable nozzle geometry, in the case of extrusion). In contrast to tube bundle reactors or heat exchangers, in a block, the space in the body between the channels is always filled by a solid material. Preferably, the block consists of one or several metals.

The term "predetermined" means that, for example, a number of different catalysts or catalyst precursors are applied to a tube bundle reactor or heat exchanger in such a way that the distribution of the different catalysts or catalyst precursors among the individual tubes is recorded and can later be retrieved, for example to determine the activity, selectivity and/or long-term stability of the individual catalysts, to permit unequivocal matching of specific measurement values with specific catalyst compositions.

Preferably, the catalysts or their precursors are produced and distributed to the different tubes

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of the tube bundle reactor in a computer-controlled manner, wherein the corresponding composition of a catalyst and the position of the tube in the tube bundle reactor, to which the catalyst or catalyst precursor are applied, is stored in the computer and can later be retrieved. The term "predetermined" is therefore used to distinguish this case from a random or statistical distribution of the generally different catalysts or catalyst precursors among the tubes of a tube bundle reactor.

The array according to this present invention of, preferably inorganic, heterogeneous catalysts and/or their precursors can be produced by using different procedures:

Procedure a) comprises the following steps:

a1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursor and possibly of dispersions of inorganic carrier materials,

a2) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the solutions, emulsions and/or dispersions,

a3) simultaneous or successive coating of the channels of the body with the solutions, emulsions and/or dispersions, wherein in each channel, a predefined quantity of the solutions, emulsions and/or dispersions is applied to obtain a predefined composition, and

a4) possibly the heating of the coated body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

Procedure b) comprises the following steps:

b1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursors and possibly of dispersions of inorganic carrier materials,

b2) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the solutions, emulsions and/or dispersions,

b3) simultaneous or successive coating of the catalyst carriers present in the channels of the body with the solutions, emulsions and/or dispersions, wherein in each channel, a predefined quantity of the solutions, emulsions and/or dispersions is added to obtain a predefined composition on the catalyst carriers, and

b4) possibly the heating of the body with the coated catalyst carriers in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

Procedure c) comprises the following steps:

c1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursors and possibly of dispersions of inorganic carrier materials,

c2) the mixing of predetermined quantities of the solutions, emulsions and/or dispersions and possibly of precipitating agents in one or several reaction vessels operated in parallel,

c3) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the resulting mixture(s),

c4) the coating of one or several predetermined channels of the body with the mixture or several mixtures,

c5) the repetition of steps c2) through c4) for other channels of the body, until the channels have been coated with each predetermined catalyst and/or catalyst precursor composition, and

c6) possibly the heating of the coated body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

Preferably, it comprises the following steps:

c1) the production of solutions of elemental compounds of the chemical elements present in the catalyst chemical elements, except for oxygen, and possibly of dispersions of inorganic carrier materials,

c2) the mixing of predetermined quantities of the solutions and/or dispersions and possibly of precipitating agents in one or several reaction vessels operated in parallel, resulting in the precipitation of the chemical elements contained in the catalyst,

c3) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the resulting suspension,

c4) the coating of one or several predetermined tubes of the tube bundle reactor or heat exchanger with the suspension,

c5) the repetition of steps c2) through c4) for different tubes of the tube bundle reactor or heat exchanger, until the tubes have been coated with the respective predetermined catalyst compositions,

c6) the heating of the coated tube bundle reactor or heat exchanger, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts.

Procedure d) comprises the following steps:

d1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the chemical elements contained in the catalyst and/or catalyst precursors and possibly of dispersions of inorganic carrier materials,

d2) the mixing of predetermined quantities of the solutions, emulsions and/or dispersions and possibly of precipitating agents in one or several reaction vessels operated in parallel,

d3) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the resulting mixture(s),

d4) the coating of catalyst carriers contained in one or several predetermined channels of the body with the mixture or one or several of the mixtures,

d5) the repetition of steps d2) through d4) for other (generally meaning not yet coated) catalyst carriers in the channels of the body, until (preferably all) catalyst carriers present in the channels of the body have been coated with the respective predetermined (generally different) catalyst and/or catalyst precursor compositions, and

d6) possibly the heating of the body with the coated catalyst carriers in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

In this context, the adhesiveness of the channels (e.g. the inner surface of the tubes) of the body or the catalyst carrier can be increased prior to coating by chemically, physically or mechanically pretreating the interior walls of the channels (e.g. internal tubes) or the catalyst carriers or by applying an adhesive layer. This applies in particular to procedures a) and c) and b) and d), respectively.

Procedure e) comprises the following steps:

e1) the production of different heterogeneous catalysts and/or their precursors in the form of full contacts with a predetermined composition,

e2) the application of always one or several of the heterogeneous catalysts and/or their precursors with a predetermined composition to always one or several predetermined channels of the body in which the heterogeneous catalysts are protected from falling out.

e3) possibly the heating of the body with the heterogeneous catalysts and/or their precursors in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

Procedure f) comprises the following steps:

f1) coating and possibly heating of predetermined catalyst carriers for the production of predetermined carrier catalysts in the manner defined above in procedures b) and/or d) outside of the body,

f2) adding the carrier catalysts to predetermined channels of the body,

f3) possibly the heating of the filled body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

Preferably, the external shape of the carrier catalysts corresponds at least largely, preferably approximately or completely, to the shape of the interior of the channel in the body.

The invention also concerns inorganic heterogeneous catalyst arrays which can be obtained by using one of the above procedures. The arrays can also be produced by combining any of the above procedures.

The procedures are suitable for the production of a large number of catalyst systems, as described for example in G. Ertl, H. Knözinger, J. Weitkamp, Editors, "Handbook of Heterogeneous Catalysis", Wiley - VCH, Weinheim, 1997.

In addition, the invention concerns a procedure g) for the determination of catalytic properties, in particular the activity, selectivity and/or long-term stability of the catalysts described above as well as below in the description of an array, comprising the following steps:

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g1) possibly activating the catalysts in the body,
g2) controlling the temperature of the body to reach a desired conversion temperature,
g3) conducting a liquid reagent or a liquid reaction mixture through (one, several or all) channels of the body,
g4) (preferably separately) removing the converted fluids from individual or several bundled channels of the body,
g5) (preferably separately) analyzing the converted fluids removed,
g6) possibly comparatively interpreting the analytic results of several analyses.

In a preferred embodiment of the procedure, after setting the body to a first conversion temperature in step g2), steps g3) through g6) are performed successively for several different liquid reagents or liquid reaction mixtures, wherein always one purging step with a purging gas is carried out between these steps, and the temperature of the body can then be set to a second conversion temperature, at which the above conversions can be repeated.

At the beginning of the analysis, the collected gas stream of the entire array can be analyzed to detect conversion in the first place.

Afterwards, in case a conversion has occurred, the discharges of the individual tubes or several tubes can be analyzed to determine the optimal catalyst with a minimum number of analytic processes.

Gas can be conducted through individual tubes or several or all tubes together.

Preferably, the liquid reagent or liquid reaction mixture is a gas or gas mixture.

The invention permits the automated production and catalytic activity testing for the purpose of mass screening of heterogeneous catalysts for chemical reactions, in particular for reactions in the gas phase, especially particularly for partial oxidations of hydrocarbons in the gas phase with molecular oxygen (gas phase oxidations).

Reactions and/or conversions suitable for testing purposes are described in G. Ertl, H. Knözinger, J. Weitkamp, editors, "Handbook of Heterogeneous Catalysis", Wiley - VCH, Weinheim, 1997, where examples of suitable reactions are mainly listed in volumes 4 and 5 under the numbers 1, 2, 3, and 4.

Examples of suitable reactions are the decomposition of nitrogen oxides, ammonia synthesis, ammonia oxidation, the oxidation of hydrogen sulfide to sulfur, the oxidation of sulfur dioxide, the direct synthesis of methylchlorosilanes, oil refining, the oxidative coupling of methane, methanol synthesis, the hydration of carbon monoxide and carbon dioxide, the transformation of methanol to hydrocarbons, reformation of catalytic activity, catalytic cracking and hydrocracking, coal gasification and liquefaction, fuel cells, heterogeneous photocatalysis, the synthesis of MTBE and T isomerizations, alkylations, aromatizations, dehydrations, hydrations,

hydroformylations, selective and/or partial oxidations, aminations, halogenations, nucleophile aromatic substitutions, addition and elimination reactions, oligomerizations and metathesis, polymerizations, enantioselective catalysis, and biocatalytic reactions.

This present invention shall be explained in more detail below by referring to preferred embodiments.

Production of the Inorganic Heterogeneous Catalyst Arrays

First, two or several, preferably 10 or more, very particularly preferably 100 or more, in particular 1000 and more, especially 10000 or more fluid base mixtures (hereinafter referred to as "mixtures") are produced, which contain selected chemical elements of the periodic system, in the form of solutions, emulsions and/or preferably suspensions (dispersions), wherein the mixtures produced in general differ in terms of their chemical composition or concentration. To test reproducibility, several mixtures of the same composition can also be used.

In general, the fluid mixtures contain a fluid chemical component which is used as a solvent, emulsifier or dispersing agent for the other components of the mixture. As solvents or dispersing agents, organic solvents, emulsifiers and/or water, preferably water, are used.

In addition to the chemical elements of the solvent or dispersing agent, the fluid mixtures contain one or several, preferably two or several, particularly preferably three or several chemical elements; in general, however, there are no more than 50 different chemical elements with a quantity of more than 1 percent by weight each. Preferably, the chemical elements are present in the mixtures in a very intimate mix, e.g. in the form of a mixture of different mixable solutions, intimate emulsions with a small drop size and/or preferably as a suspension (dispersion) containing the respective chemical elements in general in the form of a fine-part precipitation, e.g. in the form of a chemical mixed precipitation. The use of sols and gels, in particular those containing the respective chemical elements in a largely homogeneous distribution and preferably those displaying favorable adhesiveness and flow for subsequent coating, has been found to be particularly beneficial. As base compounds for the selected chemical elements, essentially the elements themselves, preferably in a finely distributed form, as well as all compounds containing the selected chemical elements in a suitable manner, such as oxides, hydroxides, oxide hydroxides, inorganic salts, preferably nitrates, carbonates, acetates and oxalates, metal organic compounds, alkoxides, etc., can be used. The corresponding base compounds can be used in solid form, in the form of solutions, emulsions, and/or in the form of suspensions.

Preferred element compounds, in particular catalytically active metals, are water-soluble oxides, hydroxides or salts with organic or inorganic acids. Active metals are preferably found in the B series of the periodic system of the elements, for example in the 5. and 6. B series for oxidation catalysts and in the platinum group for hydration catalysts. The procedure according to this present invention also permits the screening of elements which have not yet been

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considered to be catalytically active (untypical elements), in particular metals or metal oxides.

In addition, the fluid mixture can contain other compounds which impact the adhesive properties and the flow behavior of the fluid mixture on the channel's and/or the tube's interior side or catalyst carrier and therefore the coating properties of the fluid mixture. Ethylene glycol or glycerin, as described in DE-A 44 42 346, for example, and e.g. maleic acid copolymers shall be mentioned as organic compounds, and as inorganic compounds, e.g. SiO2, Si organic compounds or siloxanes shall be specifically pointed out.

In addition, the mixtures can contain inorganic carrier materials known from prior art, such as Al_2O_3, ZrO_2, SiO_2, Y_2O_3, TiO_2, active carbon, MgO, SiC or Si_3N_4, which in general increase the surface accessible for catalysis of the catalytically active chemical elements contained in the mixture, which, in addition, can impact the catalytic properties of the resulting active masses and which also can influence the adhesive or flow properties of the resulting mixture. Generally speaking, this yields coatings which contain the preferably oxidic, nitridic or carbidic carrier material in addition to the actual catalytic material. While mixing the components or during subsequent heating of the coating, however, the aforementioned carrier material can also react with the chemical elements used in the process to yield a new solid body material.

Furthermore, the mixtures used can additionally contain an inorganic and/or organic binding agent or a binding system which stabilizes the mixture used. For that purpose, e.g. binding agents or binding systems containing metal salts, metal oxides, metal oxide hydroxides, metal oxide hydroxide phosphates and/or eutectic compounds which melt at the application temperature of the catalyst.

In addition, the mixture can be set to a defined pH range by adding acids and/or bases. In many cases, pH neutral suspensions are used. For that purpose, it is advantageous to set the mixture to a pH value between 5 and 9, preferably between 6 and 8. Special results can be obtained by using the procedure according to this present invention in case the mixture has a high percentage of solids of up to 95 percent by weight, preferably between 50 and 80 percent by weight, while its viscosity is low. In the case of insufficient precipitation, precipitating agents such as ammonia can be added.

In a preferred embodiment of this present invention, the mixture is stirred after and in general also during production, and its flow is measured on an ongoing basis, although at least at the end of production. This can be carried out by e.g. measuring the electric current requirement of the stirrer assembly. Based on this measurement, the viscosity of the suspension can be set, e.g. by adding further solvents or thickening agents, to yield optimal adhesion, coating thickness and coating thickness uniformity on the interior wall of the tube or auxiliary carrier (catalyst carrier) to be coated.

As a basic rule, the invention is not limited to specific catalyst materials and catalyst compositions. The mixture can be produced in parallel or successively and is generally

prepared in an automated manner, e.g. by means of a pipetting device or pipetting robot or also by using an ink jet procedure, as described, for example, in US 5,449,754.

To coat the tubes of the tube bundle reactor or heat exchanger as per variation a) of the procedure, solutions, emulsions or suspensions of individual elements or element compounds can be applied separately or successively to the tubes. Simultaneous application can be carried out, for example, by means of a modified ink jet (ink jet printer printing head) with separate feeds for the individual solutions, emulsions or suspensions and which permits simultaneous spraying. Compared with this variation a) of the procedure, variation b) of the procedure is preferred, which is in particular carried out as described below:

To produce the catalysts or their precursors, solutions, emulsions and/or suspensions of the required elements are initially prepared in separate vessels. Frequently, these are metal salt solutions, for example nitrates. From the separate solutions, the quantities required for the production of a catalyst or catalyst precursor are transferred to a small separate reaction vessel in the desired quantities, where the components are thoroughly mixed. Dosing can be performed for example by means of a pipetting device or an ink jet. Once the components are mixed, the components may react or precipitate. By means of precipitating agents such of ammonia, a precipitation is caused or completed, as a result of which in many cases, a suspension of the mixed catalyst precursor material is obtained.

Since the suspension is supposed to have a suitable viscosity to allow its application to and distribution in a tube of the tube bundle reactor and ensure the most uniform distribution possible and largely well-bonded distribution of the catalyst or catalyst precursor on the tube's interior wall, if necessary, the suitable viscosity of the suspension can, as described above, set to the desired value by using further additives. The suspension can be removed from the reaction vessel, for example by means of pipets, and the suspension can be distributed in the tube, as described, by splashing or spraying. In this case, the reaction vessel can be partially or fully emptied. Several reaction vessels can be operated in parallel, or one reaction vessel can, once partially emptied, be refilled with other components to obtain a modified composition.

The coating with the prepared mixtures is preferably carried out by spraying of the different parts of a, in particular, metallic tube reactor or heat exchanger, in particular the interior walls of the tubes of (preferably metallic) reaction tubes of a tube bundle reactor, with a coating with a thickness of between 10 and 2000 μm, wherein in general, each tube is coated with a mixture of different compositions (to check reproducibility, several mixtures of the same composition can also be used in several tubes).

To check coating thickness effects (such as transport effects), the same catalyst compositions can also be applied with different coating thicknesses to different tubes.

In another variation of the invention, auxiliary carriers (preferably metallic or ceramic tubes) are

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used which, after or preferably prior to their insertion into the reaction tubes of a tube bundle reactor, have been coated with the fluid mixture.

The parts of the preferably metallic, heat exchanger, which have been coated with the fluid mixture prepared prior thereto are preferably the interior walls of tubes of preferably metallic tube bundle reactors. The reaction tubes of the tube bundle reactor can have any desired profile, although they generally have a round and, in particular, a circular cross section. The internal diameter is preferably between 0.2 and 70 mm, particularly between 1 and 25 mm, and very particularly between 3 and 10 mm. The tube bundle reactor can have up to 30,000 reaction tubes or more, preferably between 10 and 20,000, particularly preferably between 100 and 10,000 reaction tubes, each of which is generally coated with a different composition.

The coating with fluid mixtures can be applied by sponging, dip-coating, brushing, spin-coating, spraying and/or dipping. Additionally, the mixture can be poured into the individual tubes and centrifuged at 200 to 1000 rpm, preferably at 300 to 800 rpm. In a preferred embodiment, the coatings are produced on the interior side of the reaction tubes through spray deposition of the aforementioned fluid mixture. In this case, the spray-deposited mixture material is pressed into the roughnesses of the substrate surface, as a result of which air bubbles beneath the coating are prevented. In this case, the mixture used can also fully adhere to the coated interior side, while a part of the mixture may also drop out again, in particular in the case of low adhesion and/or low viscosity of the mixture. The auxiliary carriers to be coated, e.g. in the form of internal tubes, can be fully or only partially coated. In this case, in particular the corresponding reactor tube inlet and reactor tube outlet can not be coated by providing a suitable device, in order to avoid subsequent leaking problems with the fluid's feeding and eduction devices to be connected. A coating procedure wherein the mixture is spray-deposited in the preheated tube or such mixture is applied to the preheated tube by dipping has also been proven to be beneficial. In this case, the metallic base body is preheated, prior to spray-depositing the suspension, to between 60 and 500° C, preferably between 200 and 400° C, and particularly preferably to between 200 and 300° C, and coated at such temperature with the mixture described above. In this case, a large part of the volatile components of the mixture evaporates, forming a layer of the catalytically active metal oxide with a thickness of preferably between 10 and 2000 μm, particularly preferably between 20 and 500 μm on the preferably metallic base body. This type of production can, e.g. as described in DE-A-25 10 994, be performed with a variation where the mixture is not applied to a preheated carrier, but rather to a preheated, preferably metallic, base body.

To obtain particularly thick layers or particularly homogeneous coatings, the reaction tubes can also be coated several times in a row mesh. In this case, between the individual coatings of a reaction tube, separate drying and/or calcination and/or sintering steps can be performed. In the case of spraying, the interior walls are preferably coated by means of one or several spray lances, preferably with one or several mobile spray lances. In this case, during spraying, the spray lance is pulled, e.g. by means of an automatic device, through the tube to be coated with a defined constant or varying speed.

The thickness of the layer to be applied after drying and possibly calcination or sintering is

preferably between 10 and 2000 µm, particularly preferably between 20 and 500 µm.

In addition, prior to the coating, to the internal tube, a coupling agent is first applied, and to such coupling agent, a catalytically active top layer containing a catalytic material is then applied. By using a coupling agent, the bonding of the catalytically active top layer on the internal tube can be increased. In addition, by using a coupling agent, the pot lives can be increased. Suitable coupling agents are described above.

In addition, the bonding of the catalytic layer can be increased by chemically, physically or mechanically pretreating the internal tube prior to coating. In the case of chemical pretreatment, the internal tubes can be stained, e.g. with alkalis or preferably with acids. Furthermore, the internal tube can e.g. be roughed by blasting with a dry blasting medium, in particular emery or quartz sand, to improve adhesion. In addition, cleaning agents representing a suspension of hard particles, e.g. emery, in a dispersion fluid have also been found to be beneficial.

In addition, the coating of the preferably metallic internal tube can also contain, as components, auxiliary carriers and a catalytically active top layer containing a catalyst material, as described for example in DE-A-196 00 685. In this case, the auxiliary carrier has preferably an exterior shape which at least largely corresponds to the geometry of the surface to be coated. As auxiliary carriers, for example metallic or ceramic bodies can be used, e.g. wire meshes or tubes made from metal or ceramic. In this case, at least the auxiliary carrier and preferably only the auxiliary carrier is coated with the catalytically active top layer, and the coated auxiliary carrier is arranged in the entire interior of the reaction tube or preferably in a part of the interior of the reaction tube. In this tube-in-tube-arrangement, the outer tube can be tapered, for example on one end, to prevent the internal tube from falling out; on the other end, the projecting internal tubes can be pressed into the outer tube, for example by means of springs or a spring-loaded material.

The particularity of the procedure according to this present invention is that each auxiliary carrier in the tube bundle reactor used has generally a different composition or also a different coating thickness of the catalytic coating. In addition, the coated auxiliary carriers can easily be replaced by other auxiliary carriers with other coatings. For example, a suitable reactor construction (provision of shutoff valves, etc.) may permit the replacement of individual auxiliary carriers during reactor operation.

When heating the coated tube bundle reactor in vacuum or in a defined gas atmosphere to temperatures between 20 and 1500° C, preferably between 60 and 1000° C, particularly preferably between 200 and 600° C, and very particularly preferably between 250 and 500° C, the preferably aqueous solvent is removed from the previously applied coating by drying. At a higher temperature, in addition, the particles forming the coating can furthermore be sintered or calcinated. This process generally yields the actual catalytically active coating.

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For the purpose of temperature control, the reaction tubes are preferably enclosed by a heat carrier medium, for example by a salt melt or liquid metal such as Ga or Na. In this case, the liquid heat carrier medium is preferably supplied and removed at opposite locations of the tube bundle reactor, e.g. by means of a pump, for subsequent conduction over a (e.g. air-cooled) heat exchanger for heating or cooling. On one hand, the heat carrier medium ensures that the temperature for drying, for the possibly following sintering of the coating and for the subsequent fluid phase test reaction is reached in the reaction tubes. On the other hand, the heat carrier medium removes the quantity of heat produced during the subsequent test reaction, as a result of which, along the catalyst coating, the formation of so-called hot spots, which locally have a higher temperature than in remainder of the catalyst coating, is suppressed.

This type of reaction design ensures that the heat generated during the reaction is removed in an excellent manner, as a result of which virtually no more hot spots occur.

In another embodiment of the invention, the space located between the reaction tubes is filled with a solid material, preferably a metal, or with a solid metal alloy. In this case, the tube bundle reactor ends in a material block as described above, in particular a metal block with channels or boreholes. The internal diameter of the boreholes corresponds to the internal diameter of the reaction tubes of the tube bundle reactor.

It is also possible to produce different heterogeneous catalysts in the form of full contacts or carrier catalysts by using prior art procedures, for example combinatorial procedures, with a predetermined composition, and always apply one of these previously prepared heterogeneous catalysts to always one or several predetermined tubes of the tube bundle reactor or heat exchanger. In this case, the types of molding bodies known from prior art can be used. For each individual tube, the filling height or the inert content of a filling can be varied, or other filling parameters can be set.

The catalysts are tested by converting liquid reagents or reaction mixtures which are generally available in liquid or preferably gaseous form. Oxidation catalysts are preferably tested by parallel or successive application to individual, several or all tubes of the coated tube bundle reactor of a gas mixture consisting of one or several saturated, unsaturated or multiply unsaturated organic educts (e.g. hydrocarbons, alcohols, aldehydes, etc.), oxygen-containing gas (e.g. air, O_2, N_2O, NO, NO_2, O_3) and/or e.g. H_2, and possibly an inert gas, e.g. nitrogen or a noble gas, at temperatures between 20 and 1200° C, preferably between 50 and 800° C, particularly preferably between 80 and 600° C, wherein by means of a suitable device, the parallel or successive separate removal of the respective gas streams of individual, several or all reaction tubes of the tube bundle reactor is ensured.

Through the reaction tubes of the tube bundle reactor, which are usually coated with different compositions, for example a gas mixture from e.g. an oxygen-containing gas (e.g. air, O_2, N_2O, NO, NO_2, O_3) and/or H_2 and the organic educt to be converted is conducted. In addition to the aforementioned gaseous substances, however, other gaseous substances, such as

substances containing Cl or P, may also be present. In this case, the gas mixture can successfully be conducted through the individual reactor tubes; in a preferred embodiment, the gas mixture is conducted through the reaction tubes in such a way that the gas mixture simultaneously flows through all tubes. During the onset of the reaction, i.e. during the activation time of the catalytic coatings of the composition of the feeds, the temperature of the heat exchange medium or of the reaction tube, respectively, the residence time of the feeds and/or the pressure of the entire gas in the tube bundle reactor are changed. The product gases leaving the respective reaction tube, which are formed through the conversion of the reaction gases used, are drawn off, in general separately, but possibly also together, and analyzed e.g. in terms of their composition by different probes or analytic procedures, respectively.

The aforementioned gas mixture can also be applied to the coated tube bundle reactor directly after coating with the suspension (while omitting the drying and sintering or calcinating step), while in this case, the drying and possibly following sintering process is carried under the aforementioned gas mixture. In this case, the composition of the coating of the internal tube may change. In particular, oxidic coatings can partially or fully release their oxygen under highly reducing conditions or integrate oxygen into their structure under highly oxidizing conditions.

A constant gas mixture can be fed to the individual, differently coated reaction tubes of the tube bundle reactor e.g. via a gas supply hood, which can be mounted on the tube bundle reactor in an essentially gas-tight manner.

The gases used can be mixed prior to supplying them to the gas supply hood or only within the same, e.g. by means of a static mixer.

The individual reaction gases can be drawn off via a device essentially mounted in a gas-tight manner on the tube bundle reactor, with the individual reaction gases of individual, several or all reaction tubes being drawn off separately and subsequently being separately analyzed via a valve connection.

Another method to separately draw of the individual waste gases of the generally differently coated reaction tubes is to use e.g. a computer-controlled mechanically operated "breather device" with a breather line for the gas to be drawn off, which is essentially automatically positioned on, in or above the outlet of the corresponding reaction tube and which then takes a reaction gas sample. Positioning and removal of the respective reaction gases is preferably carried out in such a way that only the reaction gas to be analyzed later and no additional foreign gas penetrates the breather line from the outside. In case the breather device is positioned on the end of the reaction tube, mounting the breather line on the end of the reaction tube, e.g. by pressing the breather device onto the face of the tube reactor, in an essentially gas-tight manner is advantageous. In case the breather device is positioned in or above the outlet of the respective reaction tube, it is advantageous to suck the reaction gases

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into the breather devices by means of an underpressure created in the breather line in such a way that the volume of the reaction gases sucked in is limited so that no additional foreign gases are sucked into the breather line. In this case, positioning the breather line in the outlet of the respective reaction tube has been found to be particularly advantageous in case the end of the breather line is tapered in such a way that by inserting the breather line into the end of the respective reaction tube, the reaction gases leaving the respective reaction tube are sealed off from the external space in an essentially gas-tight manner. Once the reaction gas has been removed from the corresponding reaction tube of the tube bundle reactor, the breather device is positioned - preferably automatically - on, in or above another outlet of another reaction tube, generally the adjacent one, to once again draw off gas. This way, all waste gases of the reaction tubes can be separately accessed for sampling and subsequently analyzed. However, not only can the positioning device be moved into or above the outlet of reaction tube while the tube bundle reactor is permanently secured, but the breather line can be permanently secured during positioning while the tube bundle reactor is moved accordingly. During positioning, both the breather device as well as the tube bundle reactor can also be moved. In a preferred embodiment of the procedure, the tube bundle reactor remains unchanged, and only the breather device is moved during positioning above or onto the respective end of the reaction tubes. In another preferred embodiment of the procedure, the tube bundle reactor is rotated with respect to its axis during positioning, while the breather line, during positioning above the respective end of the reaction tubes, moves along a line in the direction of the axis of rotation of the tube bundle reactor, while in the case of positioning on the respective end of the reaction tubes, the breather device additionally moves parallel to the reactor axis. Several breather devices may simultaneously be used in sampling the different reaction gases. In addition, several tubes can also be sampled together.

In the same way as gas is drawn off via so-called breather lines, as a alternative to the gas supply hood, gas can be supplied based on the same principle, in which case the individual tubes are tested sequentially. In this case, the waste gas breather line must be positioned simultaneously with the fresh gas supply line.

The catalytic performance of the individual catalytic coatings of the individual reaction tubes can be screed through chemical analysis of the respective gas streams by using suitable methods known from prior art. In the process, the composition of the gas streams separately drawn off from the individual reaction tubes of the tube bundle reactor is separately tested by using suitable devices, e.g. based on gas chromatography with FID and/or WLD as a detector, or e.g. by means of mass spectrometry. In this case, the gas composition obtained is screened in particular in terms of its relative content of the desired product(s), and the resulting concentrations are compared with the converted educt, yielding values for the respective activity and product selectivities. In many cases, it is useful to measure the product selectivities of the individual catalysts over a prolonged period, generally ranging from a few hours to several weeks. During the selection of the most suitable catalyst coating for each reaction, it may be advisable, in order to reduce the number of gas analyses, to only determine the repeat measurements for gas compositions of selected reactor tubes which exceed a desired threshold concentration or threshold selectivity of specific products.

Once the catalytic test has been completed, the interior catalytic coatings that have been applied can be removed so that the resulting tube bundle reactor is once again ready for catalytic coating.

The catalyst coatings can be renewed by at least largely removing the old catalytically active top layer of the coating and applying a new catalytically active coating by sponging, brushing, spin-coating, spraying, and/or dipping. It is advisable to use the same coating procedure used to apply the catalytic activity coating that was just removed. In particular, the catalytically active top layer of the coating can be easily removed by blasting with a blasting medium, e.g. emery, silicon carbide, fine sand or the like. Alternatively, a treatment with water vapor or the use of chemical removal methods has also proven to be efficient.

One efficient method for removing the interior coatings - for example after catalyst testing – is to use brushing devices, e.g. analogous to a bottle brush, usually in connection with the aforementioned cleaners. It is preferred that interior coatings are at least largely removed in an automated manner.

The procedure according to this present invention can easily be performed in an automated manner by robots. Coating the tubes with the catalyst ensures optimal fluid flow, only causes little pressure drop, and prevents obstructions in the individual reaction tubes of the tube bundle reactor.

The spatial separation and clear identification of the tested coatings offers the advantage that one apparatus (tube bundle) can be used to simultaneously test a number of materials, generally the same in number as the tubes, in a less costly and more expeditious manner.

In addition, compared with other systems, e.g. aperture sheets, CVD arrays, the tube bundle reactor offers the benefit of permitting testing as close as possible to the technical process (with the scale-up ability remaining the same). A technically relevant optimization can be carried out in a very expeditious and cost-effective manner, in particular also due to the fact that a large number of catalysts can be tested in parallel/simultaneously under identical conditions.

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Claims

1. An array of heterogeneous catalysts and/or their precursors, comprising a body having preferably parallel, continuous channels and in which at least n channels contain n different heterogeneous catalysts and/or their precursors, wherein n is 2, preferably 10, particularly preferably 1000, and especially 10000.

2. An array according to Claim 1 wherein the heterogeneous catalysts are inorganic heterogeneous catalysts.

3. An array according to Claim 1 or 2 wherein the body is a tube bundle reactor or a heat exchanger and the channels are tubes, or the body is a block made from a solid material with channels.

4. Array according to one of Claims 1 through 3 wherein the heterogeneous catalysts and/or their precursors are full contacts or carrier catalysts and/or their precursors and are present in bulk form, a tube wall coating or an auxiliary carrier coating.

5. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

   a1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursor, and possibly of dispersions of inorganic carrier materials,

   a2) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the solutions, emulsions and/or dispersions,

   a3) simultaneous or successive coating of the channels of the body with the solutions, emulsions and/or dispersions, wherein to each channel, a predefined quantity of the solutions, emulsions and/or dispersions is added to obtain a predefined composition, and

   a4) possibly the heating of the coated body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

6. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

b1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the elements present in the catalyst and/or catalyst precursors, and possibly of dispersions of inorganic carrier materials,

b2) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the solutions, emulsions and/or dispersions,

b3) simultaneous or successive coating of the catalyst carriers present in the channels of the body with the solutions, emulsions and/or dispersions, wherein to each channel, a predefined quantity of the solutions, emulsions and/or dispersions is added to obtain a predefined composition on the catalyst carriers, and

b4) possibly the heating of the body with the coated catalyst carriers in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

7. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

c1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the chemical elements present in the catalyst and/or catalyst precursors, and possibly of dispersions of inorganic carrier materials,

c2) the mixing of predetermined quantities of the solutions, emulsions and/or dispersions and possibly of precipitating agents in one or several reaction vessels operated in parallel,

c3) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the resulting mixture(s),

c4) the coating of one or several predetermined channels of the body with the mixture or several mixtures,

c5) the repetition of steps c2) through c4) for other channels of the body, until the channels have been coated with each predetermined catalyst and/or catalyst precursor composition, and

c6) possibly the heating of the coated body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering

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or calcinating the catalysts and/or catalyst precursors.

8. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

   d1) the production of solutions, emulsions and/or dispersions of elements and/or element compounds of the chemical elements contained in the catalyst and/or catalyst precursors, and possibly of dispersions of inorganic carrier materials,

   d2) the mixing of predetermined quantities of the solutions, emulsions and/or dispersions and possibly of precipitating agents in one or several reaction vessels operated in parallel,

   d3) possibly the addition of coupling agents, binding agents, viscosity regulators, pH regulators and/or solid inorganic carriers to the resulting mixture(s),

   d4) the coating of catalyst carriers contained in one or several predetermined channels of the body with the mixture or one or several of the mixtures,

   d5) the repetition of steps d2) through d4) for other channels of the body, until the catalyst carriers present in the channels of the body have been coated with each predetermined catalyst and/or catalyst precursor compositions, and

   d6) possibly the heating of the body with the coated catalyst carriers in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

9. A procedure according to Claim 5 or 7 wherein the adhesiveness of the channels of the body is increased prior to the coating by chemically, physically or mechanically pretreating the interior walls of the channels or by applying an adhesive layer.

10. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

    e1) the production of different heterogeneous catalysts and/or their precursors in the form of full contacts with a predetermined composition,

    e2) the application of always one or several of the heterogeneous catalysts and/or their precursors with a predetermined composition to always one or several predetermined channels of the body in which the heterogeneous catalysts are protected from falling out.

e3) possibly the heating of the body with the heterogeneous catalysts and/or their precursors in the channels, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

11. A procedure for the production of arrays according to one of Claims 1 through 4, comprising the following steps:

f1) the coating and possibly heating of predetermined catalyst carriers for the production of predetermined carrier catalysts of the type defined in Claims 6 or 8 outside of the body,

f2) the addition of the carrier catalysts to predetermined channels of the body,

f3) possibly the heating of the filled body, possibly in the presence of inert or reactive gases, to a temperature ranging from 20 to 1500° C for drying and possibly sintering or calcinating the catalysts and/or catalyst precursors.

12. A procedure according to Claim 11 wherein the external shape of the carrier catalysts at least essentially corresponds to the form of the interior of the channel in the body.

13. An array which can be obtained by using one of the procedures according to one of Claims 5 through 12.

14. A procedure to determine the activity, selectivity and/or long-term stability of the catalysts in an array according to one of Claims 1 through 4 or 13, comprising the following steps:

g1) possibly activating the catalysts in the body,

g2) controlling the temperature of the body to reach a desired conversion temperature,

g3) conducting a liquid reagent or a liquid reaction mixture through channels of the body,

g4) discharging the converted fluids from individual or several bundled channels of the body,

g5) analyzing the converted fluids discharged,

g6) possibly comparatively interpreting the analytic results of several analyses.

15. A procedure according to Claim 14 wherein after setting the temperature of the body to a first conversion temperature during step g), steps g3) through g6) are carried out one after the other for several different liquid reagents or liquid reaction mixtures, wherein a purging

step with a purging gas is performed between each step, and the body can then be set to a second conversion temperature, at which the above conversions can be repeated.

16. A procedure according to Claim 14 or 15 wherein the liquid reagent or liquid reaction mixture is a gas or a gas mixture.

17. A procedure according to one of Claims 14 through 16 wherein the conversion is a gas phase oxidation.

18. A procedure according to Claim 17 wherein a reaction mixture containing molecular oxygen is used.

19. A procedure according to Claim 6 or 8 wherein the adhesiveness of the catalyst carrier in the body is increased prior to coating by chemically, physically or mechanically pretreating the catalyst carrier or by applying an adhesive layer.

20. A procedure according to one of Claims 5 through 12 and 14 through 19 wherein the procedures are automated.